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Table of Contents

1.0 Introduction 1
2.0 Study Area Geological Setting 3
3.0 Sample Collection, Processing and Analytical Methods 4
3.1 Reproducibility and Precision of Standards 4
3.2 Limit of Detection 6
4.0 Results and Surficial chemostratigraphy 6
6.0 Acknowledgements 7
7.0 References 7

1.0 Introduction

Over the past 20 years the Geological Survey of Canada (GSC) and the Ontario Geological Survey (OGS) have carried out numerous studies on the glacial sediments of southern Ontario (Fig. 1). Much of this work has focused on sequence stratigraphy and basin analysis of sediments within this region, however, there remains a lack of information on the regional geochemistry of these sediments. Results from such studies are crucial for defining chemical and related mineralogical variations within sediments and supplements sediment description, grain size data, downhole geophysical and stratigraphic correlations. It also provides a geochemical baseline for interpreting the ambient chemistry of waters contained within these sediments. Geochemical data also provides the opportunity to establish a chemostratigraphic framework that complements other stratigraphic correlation techniques, such as lithostratigraphy, event stratigraphy, and biostratigraphy.

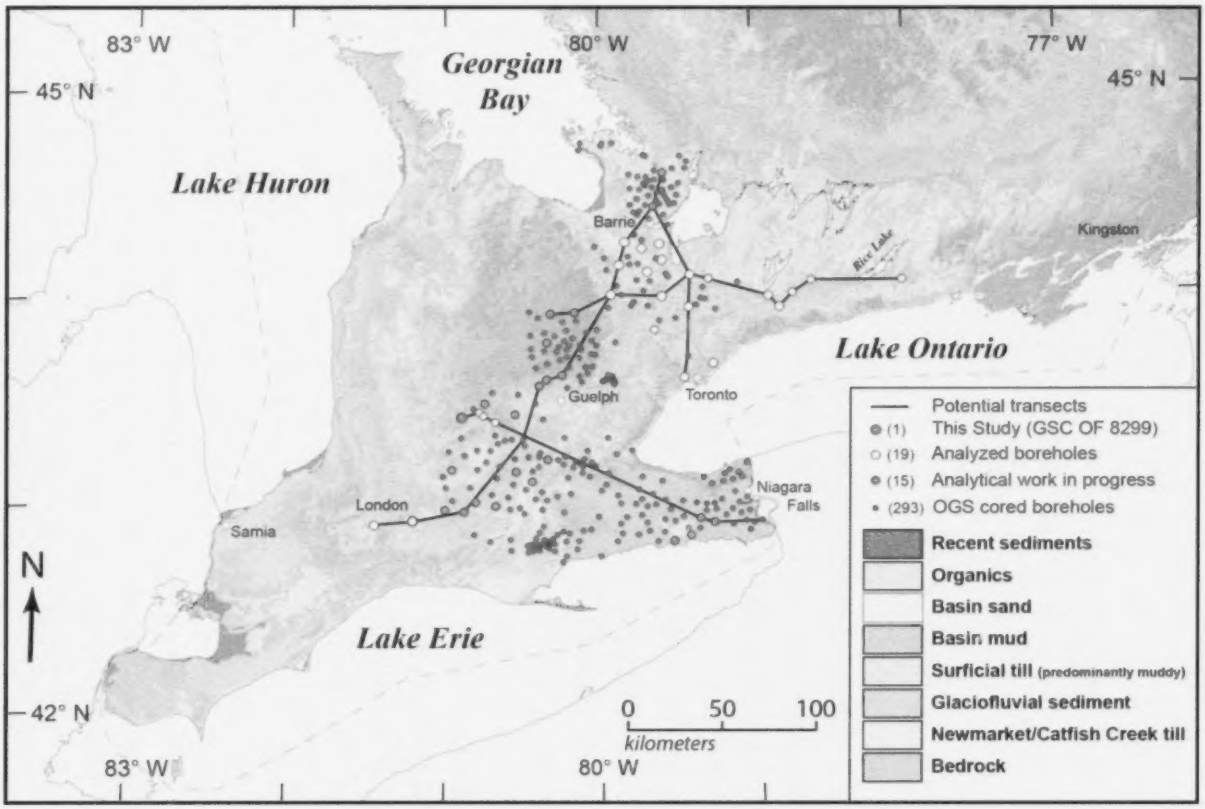

Figure 1: Location of the Gads Hill borehole in relation to other chemostratigraphically analyzed OGS and GSC cored borehole sites. Conceptual transects for this study shown as solid lines. Surficial geology of southern Ontario modified from Barnett et al., (1991).

For groundwater studies, the collection of sediment geochemistry data is often beyond the scope and budget of many programs and is generally not included as part of routine data collection. Portable X-ray fluorescent (pXRF) spectrometry has proven to be a successful tool for characterizing the chemostratigraphy of glacially derived sediments (e.g. Crow et al., 2012; Knight et al., 2015a, 2015b) as well as improving the interpretation of downhole geophysics, micropaleontology results, and pore water geochemistry (Medioli et al., 2012). Data collected using this method has now become a routine part of borehole studies within the Groundwater Geoscience Program at the GSC (Knight et al., 2015a, 2015b, 2012). To eliminate the nugget effects of sand- and gravel-sized grains common in unconsolidated glacial sediment, samples are sieved to <0.074 mm (very fine sand, silt, and clay) size fraction. The analysis on this size fraction provides fundamental information used to define chemical and mineralogical variations within aquifers and aquitards.

The objective of this Open File is to publish geochemical data for 40 samples retrieved from a borehole drilled in 2010 in Perth County, located west of Waterloo, Ontario (Fig. 2) and associated QA-QC data collected using a pXRF spectrometer. Results and simplified stratigraphic units are plotted in graph form along with downhole sand, silt and clay content.

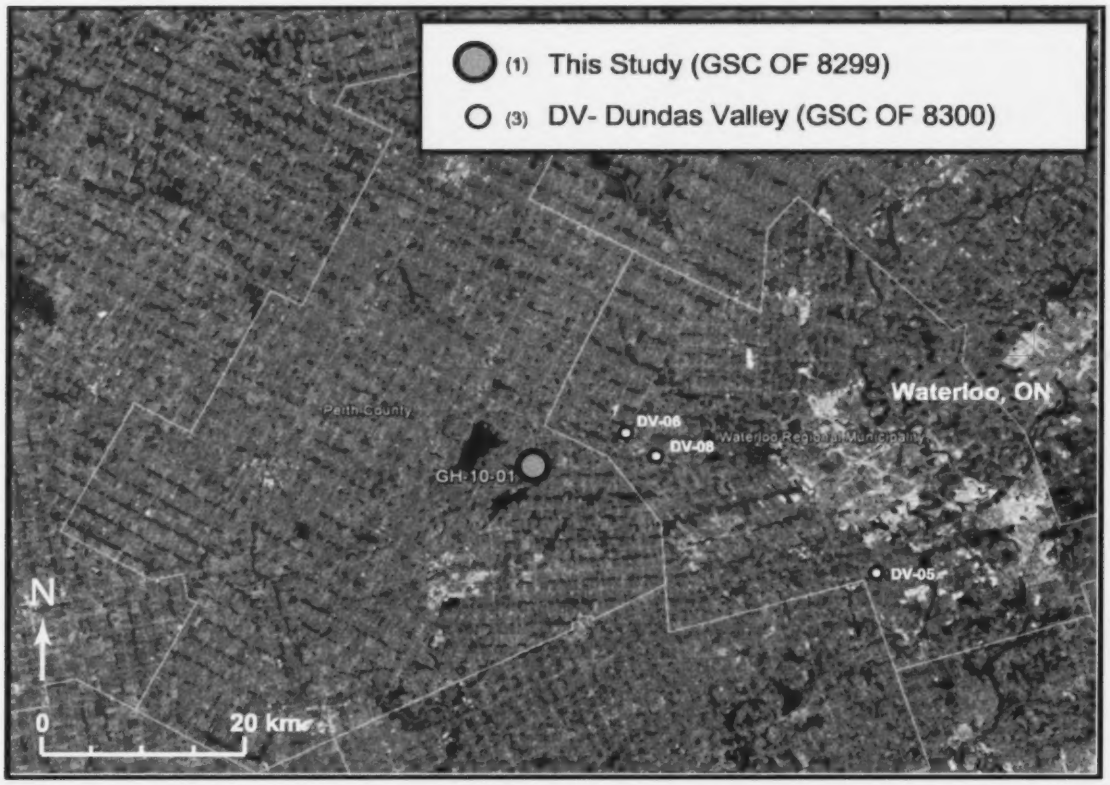

Figure 2: Location of the Gads Hill borehole and nearby boreholes drilled by the OGS and analyzed chemostratigraphically by the GSC. Image from Google Earth, 2017.

2.0 Study Area Geological Setting

The Gads Hill borehole is located on the Gads Hill moraine west of Waterloo, ON (Fig. 2). Elevation (m.asl), easting and northing coordinates (UTM NAD 83 - Zone 17) are provided in Table 1.

Table 1 – Borehole location and elevation.

Borehole ID	Depth (m)	Number of Samples	Easting	Northing	Elevation (m.asl)
GH-10-01	56.95	40	509313	4812153	~377

The borehole intersects 4 till units (Stratford Till, Tavistock Till, Catfish Creek Till and an older till overlying bedrock) each separated by glaciolacustrine sediment sequences. The moraine was first recognized by Karrow in 1967 and further described within an Ontario Geological Survey report on the Quaternary geology of the Stratford-Conestogo area (Karrow, 1993). It was constructed during a still stand in the overall retreat of the Lake Huron lobe during the Port Bruce Phase. Although the surface till in this area is mapped as Stratford Till, Karrow (1993) was of the opinion that the moraine is palimpsest and associated with the older Tavistock Till.

Older Deposits

The basal sediment in the borehole consists of approximately 4 m of a dense, silty to sandy till with thin interbeds of gravel and sandy gravel overlain by approximately 12 m of nonglacial lacustrine and alluvial deposits containing organic matter radiocarbon dated at 23.4 and 36.0 ^{14}C ka BP. The age of the lower till is not known however an Illinoian age is suspected.

Catfish Creek Till

Approximately 18 m of a dense, silty to sandy and stony till, likely correlative with the Catfish Creek Till, overlies the basal sedimentary sequence. The till, first named by de Vries and Dreimanis (1960) at its type-section south of London, Ontario, is attributed to the main Late Wisconsin glaciation when ice advanced into southern Ohio 17-23 ka BP (Karrow 1988). The till is generally overconsolidated and is commonly referred to by water well drillers as hardpan. Pebble fabrics from subglacial facies generally indicate a southwesterly ice flow however early and late lobate facies of the till have been recognized regionally across southwestern Ontario. Pebble counts indicate a predominance of dolostones consistent with a northeastern source area as well as a number of easily recognized lithologies (Gowganda tillite, jasper conglomerate) derived from the Proterozoic terrane north of Lake Huron (Karrow 1993).

Tavistock Till

Approximately 10 m of a silty to sandy glaciolacustrine sequence overlies Catfish Creek Till in the Gads Hill borehole. This sequence is in turn overlain by just over 2 m of a stone-poor, gritty clayey silt diamicton correlated to the Tavistock Till. Tavistock Till is attributed by Dreimanis and Karrow (1972) to the Early Port Bruce Phase and represents the deposit of a Huron-Georgian Bay lobe ice advance. Near Gads Hill, surface exposures of the till have a fine gritty, silty clayey texture with < 20% sand and ~30% clay. The till coarsens to the southeast. The pebble fraction is dominated by dolostones (53%), limestones (32%) and Precambrian lithologies (10%) with minor cherts and clastics (Karrow 1993). The upper portions of the till commonly contains clasts of red shale and erratics of jasper conglomerate in line with a Georgian Bay lobe source area (Karrow 1977).

Stratford Till

Approximately 7 m of silty glaciolacustrine deposits overlie the Tavistock Till in the Gads Hill borehole. These deposits are capped by approximately 2 m of a silty to sandy diamicton correlated to the Stratford Till. Stratford Till represents a thin regional unit that has been linked by Karrow (1993) to a minor and local re-advance of glacial ice, from the northwest during the overall retreat of the Huron-Georgian Bay Lobe. The Stratford till is typically stony with a sandy to silty matrix, in contrast to many of the Huron-Georgian Bay lobe deposits of the region which are typically silty to clayey. Texturally, the diamicton averages 30% sand and 18% clay with a pebble fraction dominated by limestones (47%), dolostones (39%) and Precambrian lithologies (9%) with lesser cherts and clastics (Karrow 1993).

3.0 Sample Collection, Processing and Analytical Methods

The core was drilled, logged, sampled and stored by the OGS in 2010. The borehole depths and number of samples per borehole are provided in Table 1. The OGS collected 40 samples for analysis. Samples of dried and sieved sediment were shipped from the OGS headquarters in Sudbury to the GSC at the 601 Booth St. location in Ottawa for pXRF analysis. The OGS processed sediment samples to <0.074 mm, which resulted in adding a very fine sand component to the silt and clay size fraction (<0.063 mm) normally examined by the GSC. Reprocessing the <0.074 mm samples to obtain the <0.063 mm size fraction was unnecessary as differences in size fraction from <0.063 mm to <0.074 mm do not produce results greater than the margin of error for elements with concentrations above pXRF detection limits. (Landon-Browne et al., 2017).

The processed samples were placed in 23 mm diameter plastic vials, to an approximate height of 30 mm, to obtain an infinite thickness (Knight et al., 2015c), and sealed with 4 µm thick Chemplex Prolene Thin-Film. On occasion, sample mass was limited and infinite thickness was not attainable. Sample thickness was recorded when equal to or below 5 mm. Samples below 5 mm are highlighted in light purple in Appendix A. Portable XRF data were acquired using a handheld Thermo Scientific, Niton XL3t GOLDD spectrometer equipped with Cygnet 50 kV, 2-watt Ag anode X-ray tube and a XL3 silicon drift detector (SDD) with 180,000 counts per second (cps) throughput, mounted to a test stand (Fig. 3). A 60 second dwell time per filter (Main, Low, High) was used in soil mode, in order to follow suit with previous borehole studies (Knight et al., 2015a, Knight et al., 2012, Plourde et al., 2012), for a total of 180 seconds. In mining mode 45 second dwell time was used per filter (Main, Low, High, and Light), to allow for a total of 180 seconds of analysis. Soil Mode uses Compton normalization which is recommended for elements expected to occur with < 1% concentration (trace elements). Mining Mode uses Fundamental Parameters which is recommended for elements expected to exceed >1% concentration (major elements). Table 2 presents a summary list of elements detected and their X-ray intensities.

3.1 Reproducibility and Precision of Standards

Three standards (Till-1, Till-4, and TCA 8010) and 2 blanks (SiO_2 and Teflon) were analyzed at the beginning and at the end of each analytical session and after every 10 analyses of the borehole samples. An SiO_2 blank and Teflon blank were analysed to determine the cleanliness of the pXRF window and sample stand environment. After approximately 10 analyses the operating environment (test stand) was cleaned with compressed air and Kimwipes®. Commonly the Teflon blank returns values in the 10's of ppm Ti and may return trace amounts of Mo. The Chemplex® Prolene®thin-film that separates all samples

except the Teflon blank from the spectrometer may contain trace amounts of Ca, P, Fe, Zn, Cu, Zr, Ti and Al. For the SiO_2 blank in soil mode, Cd, Hg, K, Pd, Sr, and V returned values below the recommended limits of detection (< LOD). For the SiO_2 blank in mining mode, Al returned values below the recommended limits of detection (< LOD). These elements are not listed as known impurities on the Chemplex® Prolene®thin-film and most likely represent internal detector noise. Calcium and Fe returned

Table 2: Elements and corresponding X-ray energy intensities used to determine concentrations in Mining Mode (m) and Soil Mode (s), as provided by Thermo Scientific.

Element	Line	Energy (keV)	Window Low (keV)	Window High (keV)	Filter
As	$K\alpha_1$	10.54	10.33	10.73	Main
Ba	$K\alpha_1$	32.19	31.70	32.70	High
Ca	$K\alpha_1$	3.69	3.50	3.89	Low
Cr	$K\alpha_1$	5.41	5.24	5.59	Low
Cu	$K\alpha_1$	8.05	7.84	8.24	Main
Fe	$K\alpha_1$	6.40	6.20	6.60	Main
K	$K\alpha_1$	3.31	3.10	3.49	Low
Mn	$K\alpha_1$	5.90	5.70	6.10	Main
Ni	$K\alpha_1$	7.48	7.35	7.67	Main
Pb	$L\beta_1$	12.61	12.40	12.80	Main
Rb	$K\alpha_1$	13.39	13.18	13.60	Main
S	$K\alpha_1$	2.31	2.20	2.45	Low
Sr	$K\alpha_1$	14.16	13.95	14.38	Main
Th	$L\alpha_1$	12.97	12.80	13.15	Main
Ti	$K\alpha_1$	4.51	4.21	4.70	Low
V	$K\alpha_1$	4.95	4.80	5.10	Low
Zn	$K\alpha_1$	8.64	8.49	8.83	Main
Zr	$K\alpha_1$	15.77	15.53	15.98	Main

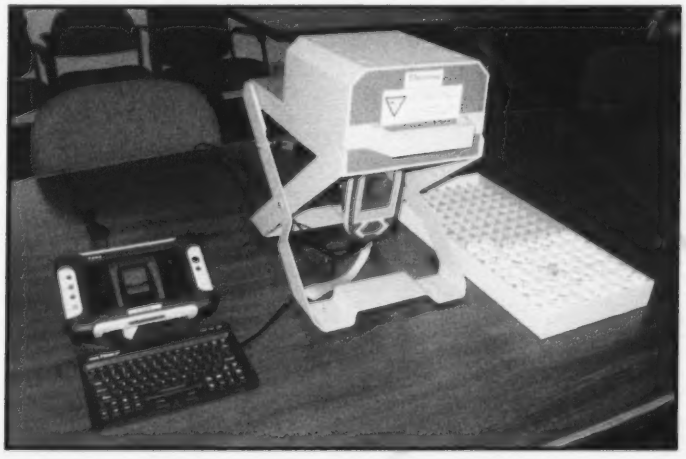

Figure 3: Example of pXRF spectrometer mounted in a test stand with micro-computer for analysis of processed sediment samples.

values above the limits of detection and may be associated with the impurities in Chemplex® Prolene® thin-film or represent contamination of the thin film. We recommend that the Chemplex® Prolene® thin-film be replaced on a regular bases to avoid contamination. A study into the precision, accuracy, instrument drift, dwell time optimization and calibration of pXRF spectrometry for reference materials including Till-1, Till-4, and TCA 8010 is available from Knight et al., (2013).

For each element detected in a given standard, the count, minimum value, maximum value, mean, standard deviation, relative standard deviation (%RSD), error and recommended values as determined by traditional wet chemistry methods are listed for both soil and mining mode for Till-1, Till-4 and TCA 8010 below each dataset collected from Gads Hill borehole in Appendix A. The percent error row contains the difference between the mean and recommended value. Low absolute values in this column indicate that the element is measured accurately; high absolute values indicate that a calibration curve is required to correct the data or that the data are not reliable.

Although care must be taken when interpreting data with a high error it may be useful to plot these elements to see if their relative changes in chemostratigraphy correlate with those of other more reliable elements. Since chemostratigraphy utilizes the relative changes in element concentration, high precision in returned values is more important than accuracy. It is also important to note that the precision and accuracy are affected by concentration. Lower concentrations, especially those near the limit of detection (LOD) tend to result in lower precision, and thus higher % RSD.

3.2 Limit of Detection

Thermo Scientific provides a list of the sensitivity or limits of detection for the pXRF (Themo Scientific, personal communication). The pXRF provides an error of each individual measurement taken throughout the 180 second analysis. For this study the error was recorded as 2 standard deviations. Some elements return results that are lower than the LOD. When this occurred, the point was plotted on the chemostratigraphy graph using the returned number however an arrow and title (LOD) was placed on the X-axis depicting the recommended LOD value.

4.0 Results and Surficial chemostratigraphy

Numerical results of elemental concentrations are presented in Appendix A as spreadsheets in Excel format for all data and as .csv files for Mining and Soil mode and for standard reference materials used in data quality control. Gads Hill stratigraphic section, lithology, grain size, and chemostratigraphy are presented graphically in .pdf format. On these graphs dashed horizontal lines correspond to the lithological breaks as defined by the OGS. In Soil Mode As, Ba, Ca, Cr, Cu, Fe, K, Mn, Ni, Rb, S, Sr, Ti, V, Zn, and Zr are detected in sufficient quantities to produce meaningful results using the pXRF spectrometer. In Mining Mode Al, As, Ba, Ca, Fe, K, Mn, Pb, Rb, S, Si, Sr, Th, Ti, Zn, and Zr are detected in sufficient quantities to produce meaningful results using the pXRF spectrometer.

Sediments in the Gads Hill borehole are generally silty to sandy with limited clay and gravel. Differences in particle size distribution are dependant on source material and depositional environments. The sedimentary sequence consists of alternating till and glaciolacustrine deposits. Although the pXRF derived geochemistry is carried out on the < 0.074 mm size fraction, there is an apparent relationship between

grain size, associated mineralogy and resulting geochemistry. The relationship between partitioned minerals and chemistry is visible in the increase in Ba, Sr and Zr content between a depth of 10-20 meters that corresponds to a decrease in silt content and an increase in sand. Due to the highly variable nature of sediments and sample distribution below 40 meters depth, the chemistry for the lower portion of the borehole is unrevealing with changes in chemical composition being associated with changes in grain size and associated mineral partitioning.

For the Catfish Creek till the upwards increase in sand content is also reflected in an increase in Ca content and a corresponding decrease in the Fe, K and S content. The abrupt change in chemistry for some elements between Catfish Creek Till and underlying deposits suggests the resultant chemical composition of the till is minimally affected by incorporation of the lower sediments into the till. The steady variation of chemical elements (i.e. Ca, Fe, K) upwards through the till sequence suggests a variation in source material from shield rocks near the base of the till to more carbonate-rich lithologies towards the top of the sequence.

Similarly, the sediments above the Catfish Creek till have a distinctive signature as displayed, for example, by the sharp increase in Sr concentrations in both mining and soil mode and S concentrations in mining mode.

6.0 Acknowledgements

Samples from the Gads Hill borehole were collected and transferred to the Geological Survey of Canada by the Ontario Geological Survey. The analytical work was carried out at GSC-Ottawa under the Aquifer Assessments and Support to Mapping, Groundwater Inventory Project of the Groundwater Geoscience Programme. This work is a contribution of the GSC-OGS Southern Ontario project on groundwater 2014-2019.

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